A Note on the Formation of Etch Pits on Crystals

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A Note on the Formation of Etch Pits on Crystals*

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Synopsis

It is shown that an etch pit on a crystal may be originated from one of the two causes. The first cause is a microscopic pit or an easily soluble minute portion or inclusion which exists accidentally and locally on the crystal surface, and the other is a dislocation existing in the crystal. In the etch pit originated from the first cause its depth is unchanged but its calibre increases as dissolution or etching proceeds (the temporary or short-time etch pit), while both the depth and calibre of the etch pit originated from the second cause increase in proportion to the etching time (the permanent or dislocation etch pit). A brief consideration is also made of the mulitiplicated etch pit as a variation of the dislocation etch pit. Experimental evidences for the considerations are presented.

I. Introduction

The etch pits or, generally, etch fiqures on crystals have long been observed and studied, and the examination of them was one of means for finding out the symmetry of a crystal in the era before the introduction of the method of X-ray diffraction, since their shapes and arrangements are in accord with the symmetry of the crystal surface on which they locate.(1) But, the problem of the formation etch pits and the problem of the dependence of their shapes upon the condition of dissolution or etching have not yet been clarified. The present note concerns with the first of these classical problems.

II. Temporary or Short-Time Etch Pits

When an ideal crystal surface, free of any imperfection, is dissolved or etched, pits with the depth of an atomic distance and the calibre of the order of a micron may be formed by thermal fluctuation. But, since these two dimensional nuclei of etch pits grow rapidly and extend over the entire of the crystal surface, macroscopically the crystal surface dissolves uniformly with the rate depending upon the condition of dissolution and thus etch pits in the usual sense are not formed. Accordingly, in order that etch pits in the usual sense may be formed, it is necessary that on the crystal surface there are originally and locally microscopic pits caused by any cause or otherwise easily soluble portions (for instance, strained portions, impurity-rich portions, and inclusions).

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* The 895th report of the Research Institute for Iron, Steel and Other Metals. The original of this report, written in Japanese language, was previously published in Nippon Kinzoku Gakkai-shi (J. Japan Inst. Metals), **21** (1957), 85.

(1) H. Baumhauer, *Die Resultate der Aetz-Methode in der Kristallographischen Forschung,* Leipzig (1894); A. P. Hones, *The Nature, Origin and Interpretation of the Etch Figures in Crystals,* New York (1927).

Now, we suppose, for simplicity, that, on a crystal surface, there is originally a hemispherical pit of the radius r_0, which is shown by ACBOA in Fig. 1 (a). We, further, represent the orientation in terms of the polar coordinates of which the pole axis is the normal $\overrightarrow{OC}$ of the crystal surface directing towards the interior of the crystal and the zero line of the azimuthal angle, φ, is a certain direction on the crystal surface, say $\overrightarrow{OA}$. When the crystal surface is dissolved, each point on the surface of the hemispherical pit displaces, towards the interior of the crystal, along the direction connecting the point and the center O of the hemi-sphere with the solution rate, $v(\theta, \varphi)$, depending upon the direction and the condition of dissolution, resulting, after a time t, a pseudo-hemispherical pit A′DC′EB′BOAA′ larger than the original pit (Fig. 1 (a)), but at the same time the crystal surface as a whole displaces, towards the interior of the crystal, along its normal $\overrightarrow{OC}$ with the characteristic solution rate v_c, so that an actually produced pit is DC′EPD.

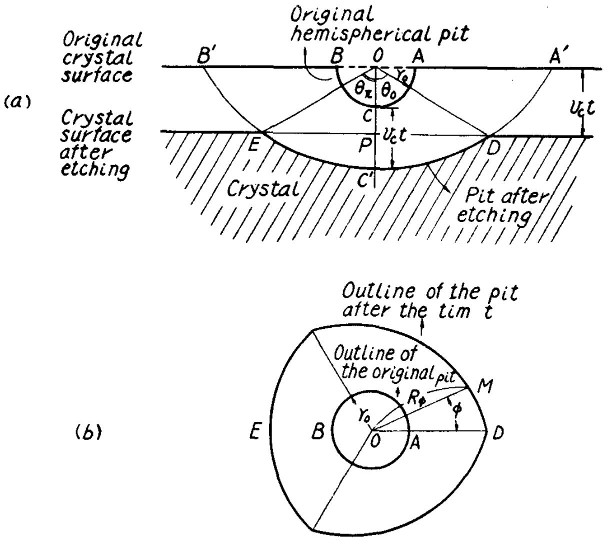

Fig. 1. Transformation by etching into a temporary etch pit of an originally hemispherical pit located on the crystal surface.

In Fig. 1 (a), if a straight line connecting the point O with a point M, lying on the line of intersection of the pit DC′EPD with the crystal surface disclosed after the time t, makes an angle θ_φ with the normal $\overrightarrow{OC}$ of the crystal surface, then the following relation holds:

$$[r_0 + v(\theta_\varphi, \varphi)t] \cos\theta_\varphi = v_c t, \tag{1}$$

from which θ_φ may be determined as a function of φ, r_0, v_c, and t. But, since actually it may be that

$$r_0 \ll v(\theta_\varphi, \varphi)t, \tag{2}$$

Eq. (1) is reduced to

$$v(\theta_\varphi, \varphi) \cos\theta_\varphi \simeq v_c, \tag{1a}$$

so that θ_φ depends on φ and v_c alone. The depth, $d\,(=\overline{\mathrm{PC'}})$, of an etch pit thus produced is always equal to that of the initial pit:

$$d = r_0, \tag{3}$$

and the length of the line connecting the point M, lying on the line of intersection of this etch pit with the crystal surface, with the geometrical center P of the line of intersection is

$$R_\varphi = [r_0 + v(\theta_\varphi,\ \varphi)\,t]\sin\theta_\varphi \simeq v(\theta_\varphi,\ \varphi)\sin\theta_\varphi\cdot t = v_c\tan\theta_\varphi\cdot t, \qquad (4)$$

so that the calibre D of this etch pit is given by

$$D = R_\varphi + R_{\varphi+\pi} \simeq v_c(\tan\theta_\varphi + \tan\theta_{\varphi+\pi})\,t. \qquad (5)$$

Thus, the calibre of the pit increases with the rate depending on the crystal surface on which it locates and on the direction in the crystal surface, so that the etch pit takes a shape characteristic to the crystal surface. It is to be noted, however, that the depth of this etch pit is invariant irrespective of the time of dissolution, as mentioned above. Accordingly, this etch pit may be observed surely as an etch pit at the beginning of dissolution of the crystal, but, at the later stage of dissolution, it may no longer be regarded as an etch pit since it becomes a very flat pit extending over the entire surface of the crystal. It may, thus, be concluded that pits located originally on the crystal surface, irrespective of their shape and size, ultimately diverge with the dissolution of the crystal. This conclusion also holds for the case where, on the crystal, there are, initially and locally, easily soluble portions or inclusions, which dissolve at the very early stage and leave pits on the crystal surface. Such etch pits will be called temporary or short-time etch pits in the following.

III. Permanent or Dislocation Etch Pits

Now, usually observed etch pits grow in depth as well as in calibre with increasing etching time. To realize such a situation it must be supposed that there are, in a crystal, easily soluble portions or defects which extend linearly and continuously and appear continuously on the crystal surface as the crystal dissolves. Defects extending linearly and continuously are dislocations.

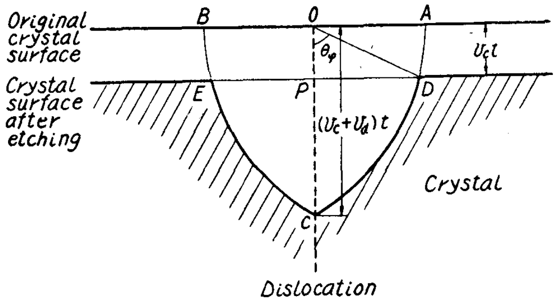

Fig. 2. Formation of a simple permanent etch pit caused by a dislocation.

Let us consider, for simplicity, a case where a dislocation exists perpendicularly to the crystal surface ($\overrightarrow{OC}$ in Fig. 2). We assume that the solution rate along the dislocation is great by an amount v_d as compared with the solution rate v_c along the same direction in the perfect portion of the crystal, while the solution rate along the direction perpendicular to the dislocation line is the same as that along the same direction in the perfect portion. Let the anisotropy of the solution rate in the dislocated portion be represented as $v'(\theta, \varphi)$. Then, when this crystal surface is dissolved for the time t, a semiellipsoid-like pit ADCEBOA, of which the major axis is $(v_c + v_d)t$ and the minor axis is $v'(\pi/2, \varphi)\,t\ (= v(\pi/2, \varphi)t)$ is formed along the dislocation line and, at the same time, the crystal surface as a whole is displaced by v_c, so that an eventually formed pit is DCEPD (Fig. 2).

In Fig. 2, let the angle which a straight line connecting the point O with a point on the line of intersection of this etch pit with the crystal surface makes with the dislocation line $\overrightarrow{OC}$ be θ_φ. Then, we have a relation.

$$v'(\theta_\varphi, \varphi) \cos \theta_\varphi = v_c, \tag{6}$$

which indicates that θ_φ depends on φ and v_c. The depth, $d(=\overline{PC})$, of this etch pit and the length, R, of a line connecting between a point on, and the center P of, the line of intersection of the etch pit with the crystal surface are given, respectively, by

$$d = v_d t \tag{7}$$

and

$$R_\varphi = v'(\theta_\varphi, \varphi) t \cdot \sin \theta_\varphi = v_c \tan \theta_\varphi \cdot t, \tag{8}$$

indicating that d and R increase with increasing etching time. Such an etch pit will be called a permanent or dislocation etch pit in the following.

When the dislocation line does not extend straightly but breaks at right angles into another type of dislocation (Fig. 3), and the dislocation etch pit formed and enlarged continuously in the part $\overline{OL}$ of the dislocation line crosses the extension $\overline{LL'}$ of the part $\overline{OL}$, the depth of the etch pit is unchanged but only its calibre increases with increasing etching time and, unless it cuts the dislocation line of the same type as the original dislocation, it gradually diverges just as the temporary etch pit mentioned before. But, if the kink of the dislocation is so small that the etch pit soon cut the dislocation line of the same type as the original dislocation ($\overline{MN}$ in Fig. 3), a new center of the etch pit is formed at this dislocation line, and both of the old and new centers co-exist for a some time, though the old center soon vanishes. Further, when the dislocation line extends obliquely to the crystal surface the axis of an etch pit caused by this dislocation also becomes oblique, namely, the bottom of the etch pit displaces sideways, resulting an eccentric etch pit. Furthermore, when the dislocation branches, there results the same number of centers as branch dislocations.

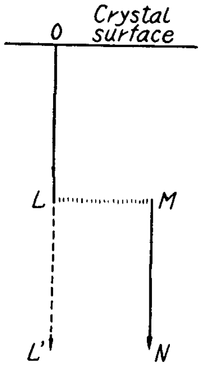

Fig. 3. Kink of dislocation.

IV. Experimental Evidence

That, as the above consideration shows, there may be, on the crystal, two kinds of etch pits, namely the temporary and permanent or dislocation etch pits, may be seen from microphotographs of (0001) surfaces of SiC crystals etched with fused sodium carbonate and with fused borax, published, respectively, by Horn(2) and

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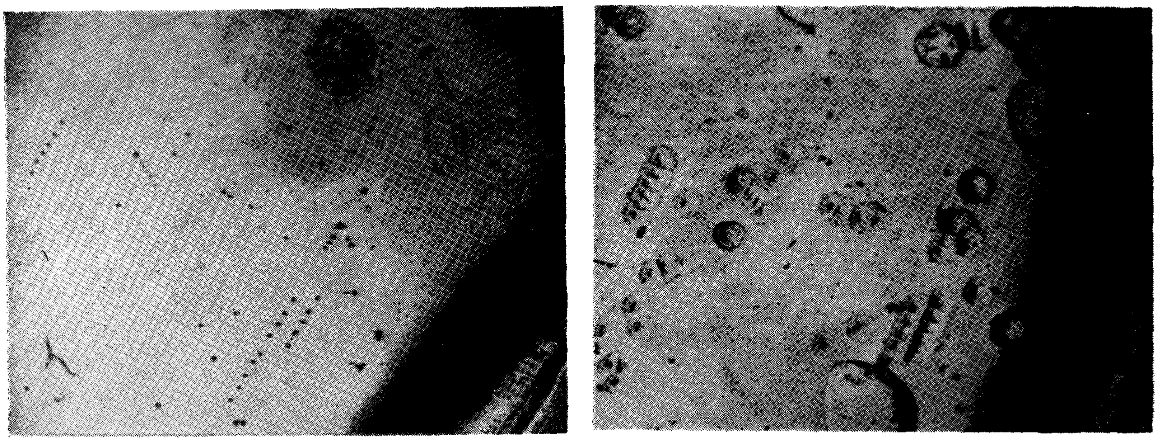
(2) F. H. Horn, Phil. Mag., **43** (1952), 1210.

by Gevers⁽³⁾ (Photos. 1 and 2). It has been shown by Horn himself that pits arranged along straight lines in Photo. 1 are the dislocation etch pits. But, there are also a number of scattered pits of a somewhat rounded shape, which may be identified as the temporary etch pits since they are flat and large as compared with the dislocation etch pits. Further, in Photo. 2 in which a dotted line shows the position of a growth spiral observed before etching, there are a hexagonal pit which is the emergence point of a screw dislocation and many shallow, rounded pits The former is the dislocation etch pit and the latter are the temporary etch pits. It may be seen that these temporary etch pits concentrate along steps of the growth spiral, which may be interpreted as due to the fact that depressions formed by the steps are easily etched.



(a) Etched for 10 min. (b) Etched for 40 min.

(c) Etched for 80 min.

Photo. 1. Process of formation of etch pits on (0001) surface of a SiC crystal etched with molten sodium carbonate (Horn⁽²⁾). ×65

One of morphological evidences for the fact that etch pits may be associated with dislocations is furmishes from an electronmicrograph of etch pits on a nearly (100) surface of aluminium crystal etched with the 1:1 mixture of aqua regia and water, which is shown in Photo. 3. Bases of these etch pits are not

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(3) G. Gevers, Nature, **171** (1953), 171.

flat but have irregular-shaped depressions, namely, portions with particularly large dissolution rate.

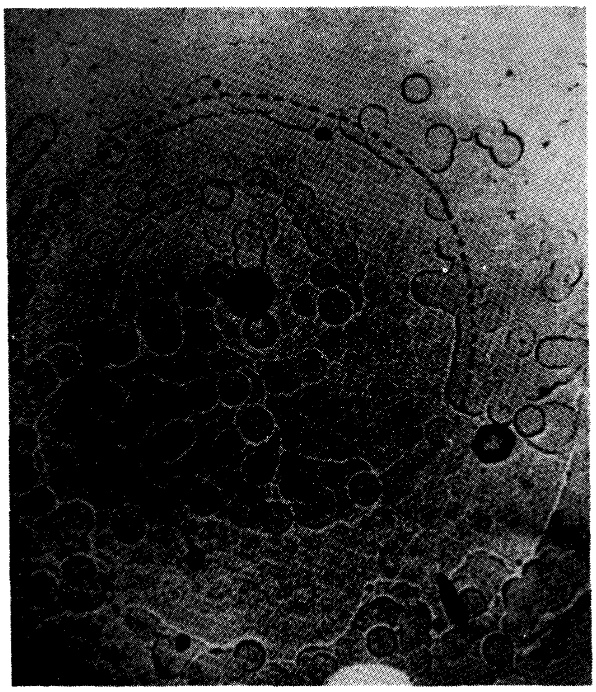

Photo. 2. Formation of etch pits on (0001) surface of a SiC crystal etched with fused borax (Gevers(3)). ×200

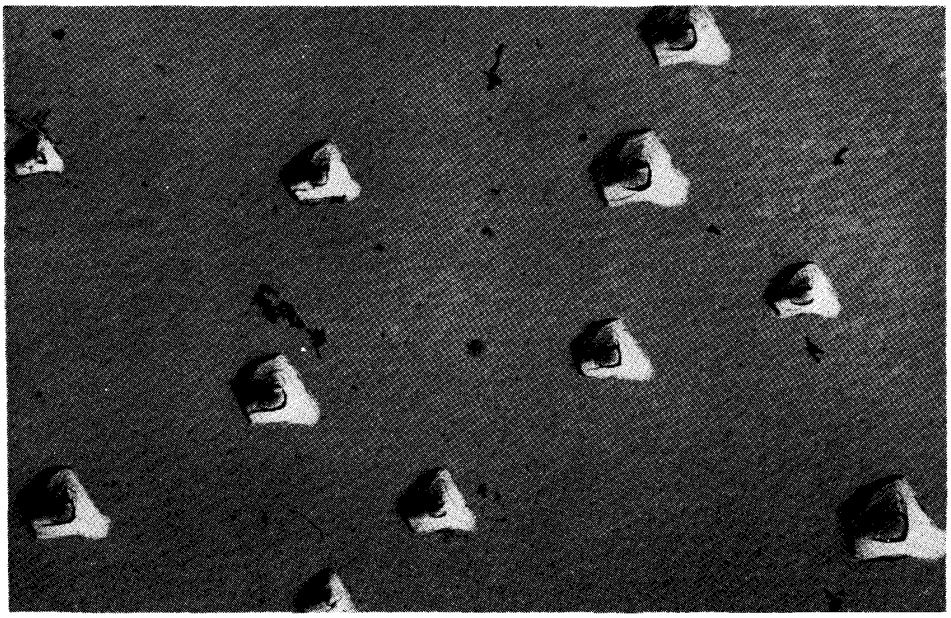

Photo. 3. Etch pits on a nearly (100) surface of aluminium crystal etched with aqua regia plus water (1 : 1). ×10,000

An example of eccentric etch pits caused by the kink of dislocation is an electronmicrograph of (111) etch pits of bismuth crystal etched with the 1:1 mixture of concentrated nitric acid and water (Photo. 4). The surface density of

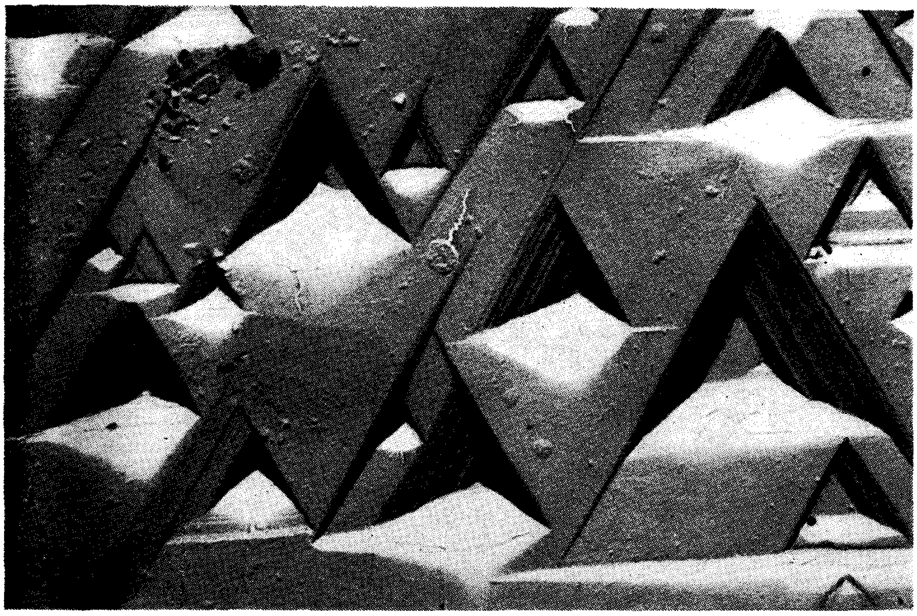

Photo. 4. Etch pits on (111) surface of bismuth crystal etched with nitric acid plus water (1 : 1). ×10,000

these etch pits is $1 \times 10^7 \mathrm{cm}^{-2}$. Eccentric etch pits were also observed on (111) surfaces of germanium crystals etched with No. 2 reagent (HF 1 + H_2O_2 1+H_2O 4 in volume) by Ellis(4) and etched with No. 3 (HNO_3 10 + HCl 10 + H_2O_2 3 in volume) and No. 4 (HNO_3 1 + HCl 1 in volume) reagents by Kikuchi and Denda(5) (Photo. 5).

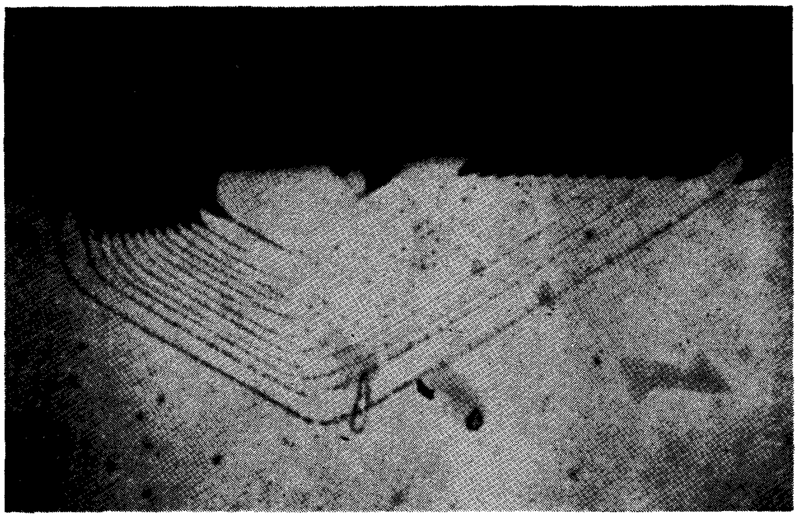

Photo. 5. Oblique etch pits on a silicon crystal. Dislocations are indicated by copper precipitates (Dash(7)).

Finally, Photo. 6 shows a beautiful example of oblique etch pits caused by dislocations extending obliquely to the crystal surface as obtained by Dash(6) with silicon crystals in which dislocations are decorated by copper precipitates.

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(4) S. G. Ellis, J. Appl. Phys., **26** (1955), 1143.

(5) M. Kikuchi and S. Denda, J. Phys. Soc. Japan, **11** (1956), 1127.

(6) W. C. Dash, J. Appl. Phys., **27** (1956), 1193.

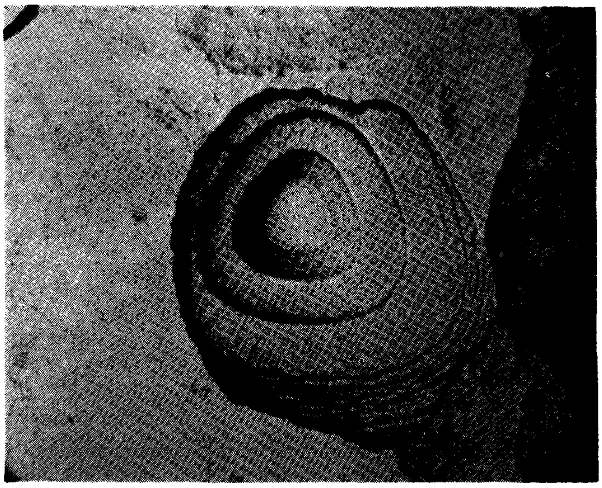

Photo. 6. Etch pit on (111) surface of germanium crystal etched with No. 4 reagent (Kikuchi and Denda(5)).

V. Multiplicated Etch Pits

Dislocation etch pits with a stepped structure are observed frequently, as seen also from Photo. 4 and Fig. 4 shown above. We may consider that such etch pits are formed as follows:— Let us suppose that there is a more or less well-defined boundary between the core of the dislocation and the perfect portion of crystal, which may be due to any cause, and that, in the core, the solution rate along the

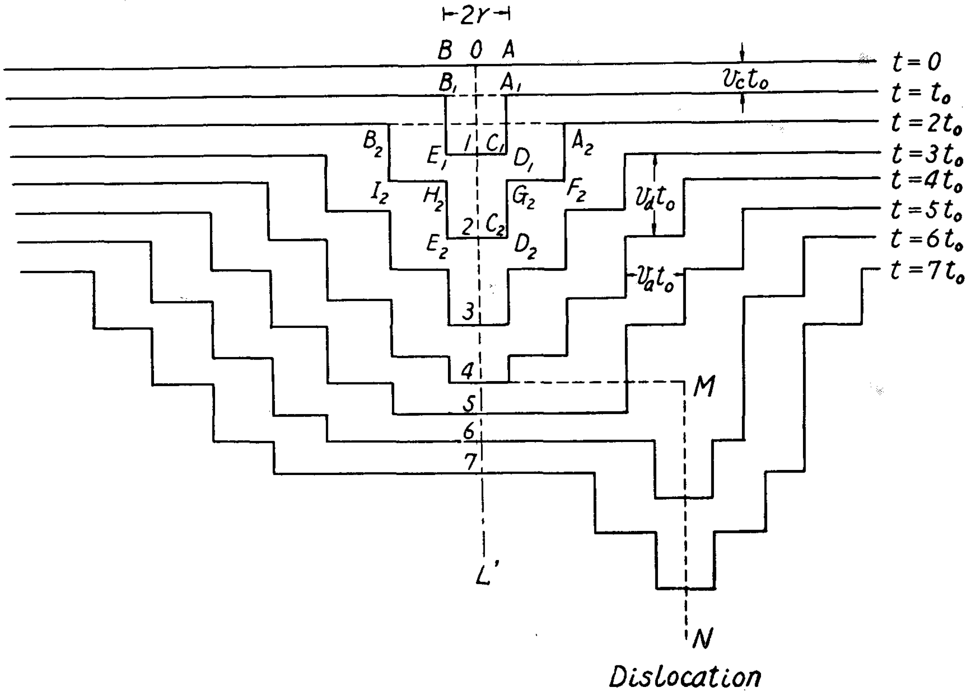

Fig. 4. Formation of a multiplicated etch pit around a dislocation line.

direction of the dislocation line is $v_c + v_d$, as in III, and that along the direction perpendicular to the dislocation line is v_w (in the portion outside the core, the solution rate along the direction normal to the dislocation is v_a ($< v_w$)). When the crystal surface, pierced normally by the dislocation of which the core radius is r_0, is etched, then, a microscopic pit ($A_1D_1C_1E_1B_1A_1$) is formed in the core of the dislocation after a definite short time t_0 ($=r_0/v_w$), as shown in Fig. 4. After the time $2t_0$, this pit is enlarged by $(v_c + v_d)t_0$ along the direction of the surface normal and by $v_a t_0$ ($v_a = 2v_c$ in Fig. 4) laterally, thus becoming a duplicated pit $A_2F_2G_2D_2C_2E_2H_2I_2B_2A_2$. The pit become a triplicated pit after $3t_0$, and a n th-multiplicated pit after nt_0, thus becoming multiplicated as long as the dislocation exists. In this multiplicated etch pit, the height of the step is $v_d t_0$ and the width of the terrace is $v_a t_0$, both being constant, while the depth d is

$$d = v_d t \tag{9}$$

and the calibre D is

$$D = 2R = 2\{r_0 + v_a(t - t_0)\}, \tag{10}$$

both increasing with increasing etching time.

When the dislocation does not extend straightly but breaks at right angles into another type of dislocation (Fig. 3), in the part $\overline{LL'}$ of the extension of the original dilsocation line, the multiplicated etch pit formed in the part $\overline{OL}$ does not change the stepped structure of its side faces but enlarges only the calibre D_b of its basal face as

$$D_b = 2(r_0 + v_a t). \tag{11}$$

Accordingly, this etch pit diverges unless it cuts again the dislocation of the same type as the original dislocation. But, if the kink of the dislocation is so small that the multiplicated etch pit soon cuts the dislocation of the same type as the original dislocation, a new center is formed at this dislocation. Etch pits in

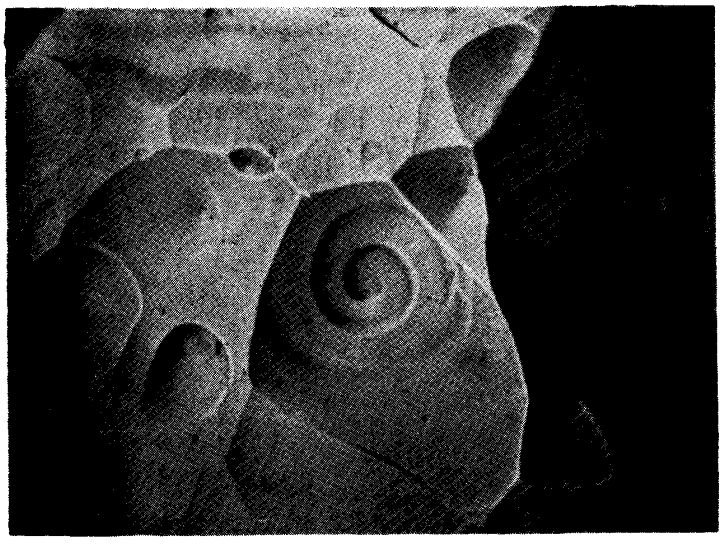

Photo. 7. Spiral etch pit on (111) surface of germanium crystal etched with the mixture of HNO_3, HF, HCl and H_2O_2 (Kikuchi and Denda(7)).

Photo. 4 and Fig. 4 may be considered to be thus formed eccentric multiplicated etch pits.

The fundamental types of dislocations are the edge and screw types. Steps of the multiplicated etch pit caused by an edge dislocation may be closed concentric rings and those of the etch pit caused by a screw dislocation may be spiral. Examples of the latter are {111} etch pits on germanium crystals etched with No. 2 reagent (by Ellis(6)) and etched with the mixture of HNO_3, HF, HCl, and H_2O_2 (Kikuchi and Denda(7)) (Photo. 7) and on silicon crystals etched with the mixture of HF, HNO_3, CH_3COOH, and KNO_3 (Matsukura and Suzuki(8)).

In closing, the author thanks to Messrs. Kikuchi and Denda who kindly provided him beautiful photographs of etch pits on germanium crystals.

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(7) M. Kikuchi and S. Denda, J. Phys. Soc. Denda, J. Phys. Soc. Japan, **12** (1957), 105.

(8) Y. Matsukura and T. Suzuki, J. Phys. Soc. Japan, **12** (1957), 976.